Detergent compositions comprising large pore size redox catalysts

Inventors: Athanasios Surutzidis, Hamilton; Robert Y. Pan, Cincinnati; Gregory S. Caravajal, Fairfield; James C. T. R. Burckett-St. Laurent, Cincinnati, all of Ohio

Assignee: The Procter & Gamble Company, Cincinnati, Ohio

Filed: Jul. 11, 1994

Related U.S. Application Data


References Cited

U.S. PATENT DOCUMENTS

3,398,096 8/1968 Das et al. ........................................... 252/95
4,430,243 2/1984 Bragg ........................................... 252/91
4,478,733 10/1984 Oakes ........................................... 252/99
4,536,183 8/1985 Namatham ........................................... 8/107
4,578,206 3/1986 Walker ........................................... 252/95
4,604,224 8/1986 Cheng ........................................... 252/91
4,623,357 11/1986 Urban ........................................... 8/107
4,626,373 12/1986 Finch et al. ........................................... 252/96
4,626,374 12/1986 Finch et al. ........................................... 252/174.13
4,655,782 4/1987 McCaillon et al. ........................................... 8/111
4,711,748 12/1987 Irwin et al. ........................................... 264/117
4,728,455 3/1988 Rerek ........................................... 252/99
5,098,684 3/1992 Kresge et al. ........................................... 423/277

ABSTRACT

Laundry and cleaning compositions which comprise large pore size redox catalysts.

11 Claims, No Drawings
DETERGENT COMPOSITIONS
COMPRISING LARGE PORE SIZE REDOX CATALYSTS

This is a continuation-in-part application of application U.S. Ser. No. 08/257,927, filed Jun. 10, 1994 abandoned.

FIELD OF THE INVENTION

The present invention relates to the use of large pore size redox catalysts in laundry and cleaning products.

BACKGROUND OF THE INVENTION

Metal-containing catalysts have been described in bleaching compositions, including manganese-containing catalysts such as those described in EP 549,271; EP 549,272; EP 458,397; U.S. Pat. No. 5,244,594; U.S. Pat. No. 5,246,621; EP 458,398; U.S. Pat. No. 5,194,416; and U.S. Pat. No. 5,114,611. These bleaching catalysts are described as being active for catalyzing the bleaching action of peroxo compounds against various stains. Several of these bleaching systems are said to be effective for use in washing and bleaching of substrates, including laundry and hard surfaces (such as machine dishwashing, general cleaning) and in the textile, paper and wood pulp industries.

It has been discovered that these metal-containing bleach catalysts, especially the manganese-containing catalysts, have the particularly undesirable property, when used with textiles, of damaging the fabric resulting in loss of tensile strength of the fibers and/or producing color damage to the fabric. Obviously, such properties for compositions is a great drawback to the general use of these compositions in the laundry area.

By the present invention, large pore size redox catalysts are included in laundry and cleaning products to provide dye transfer inhibition benefits and/or to catalyze peracid bleaching without accompanying fabric damage. The catalysts are also compatible with enzymes in such compositions. These and other advantages of the present invention will be seen from the disclosures hereinafter.

BACKGROUND ART

The use of manganese with various complex ligands to enhance bleaching is reported in the following U.S. Pat. Nos.: 4,430,243; 4,728,455; 5,246,621; 5,244,594; 5,284,944; 5,194,416; 5,246,612; 5,256,779; 5,280,117; 5,274,147; 5,153,161; 5,227,084; 5,114,606; 5,114,611. See also: EP 549,271 A1; EP 544,490 A1; and EP 549,272 A1. Bleach catalysts said to be bound to various materials are described for example in EP 544,440 A2, U.S. Pat. No. 4,711,748, EP 224,952 A, U.S. Pat. No. 4,623,357, U.S. Pat. No. 4,601,845, U.S. Pat. No. 4,536,183, and U.S. Pat. No. 4,626,373.


SUMMARY OF THE INVENTION

The present invention encompasses cleaning compositions comprising a catalytically effective amount of a large pore size redox catalyst. Such compositions preferably comprise large pore size redox catalyst in combination with enzymes and/or builders and/or bleaching agents (with or without bleach activators).

Preferred are those cleaning compositions comprising one or more enzymes, preferably comprising at least about 0.001% by weight of the compositions. Preferred are proteases, cellulases, amyloses, lipases, peroxidases and mixtures thereof.

Also preferred cleaning compositions are those that comprise at least about 1% of a bleaching agent, and optionally (but preferably) with at least about 0.1% of a bleaching activator.

Preferred compositions herein comprise at least about 1%, by weight, of a detergent builder, especially non-phosphorus builders selected from the group consisting of zeolites, layered silicates, polycarboxylate builders, and mixtures thereof.

Fully-formulated compositions herein preferably additionally comprise at least about 0.1%, by weight, of a detergent surfactant, especially surfactants selected from the group consisting of alkyl sulfates, alkyl ethoxy sulfates, polyhydroxy fatty acid amides, ethoxylated alcohols, and mixtures thereof.

Preferred granular laundry detergents provided by this invention comprise:

(a) at least about 0.001% by weight of a large pore size redox catalyst;
(b) from about 0.001% to about 5%, by weight, of enzymes selected from the group consisting of protease, cellulase, amylase, lipase, peroxidase, and mixtures thereof;
(c) from 0.1% to about 80%, by weight, of a detergent surfactant;
(d) from about 1% to about 80%, by weight, of a detergent builder; and
(e) from about 1% to about 30%, by weight, of a bleaching agent; and
(f) the balance of the composition comprising detergent adjunct ingredients.

The invention also encompasses a method for cleaning soiled surfaces, as in contacting fabrics with an aqueous medium which contains at least about 50 ppm, preferably from about 100 ppm to about 10,000 ppm, of a composition according to the above, preferably with agitation.

All percentages, ratios and proportions herein are by weight, unless otherwise specified. All documents cited are, in relevant part, incorporated herein by reference.

DETAILED DESCRIPTION OF THE INVENTION

Large Pore Size Redox Catalysts:

The present invention compositions comprise a catalytically effective amount of a large pore size redox catalyst, preferably in an amount of at least about 0.001%, more preferably from about 0.001% to about 10%, and most preferably from about 0.05% to about 5%. The term "catalytically effective amount", as used herein, means a level of the redox catalyst present in the cleaning compositions of the present invention such that the catalyst is effective for providing the desired catalytic activity in those composi-
ions, such as dye transfer inhibition and/or bleach catalyist activity. As used herein, the term “large pore size redox catalysts” means any porous material having a mean pore size of greater than about 10 Angstroms and having redox (i.e., either reductive or oxidative) catalytic properties resulting at least in part from the presence of metal bound to (under typical use conditions of the present invention compositions) or incorporated into the large pore size crystalline material. Preferred are oxidative catalysts for use in the present invention compositions.

The metal may therefore be present in the catalyst by physical interactions with the porous material, by ionic or covalent bonding, or by clusters of metals likewise bound or attached to the porous material. For example, this may include covalently bonding by reacting polyhalogenated metallolporphyrins with aminopropyl-modified porous materials, reaction of the pyridyl group of pyridyl-containing metallolporphyrins with chloropropyl-modified porous materials, silylation of porous materials with a metalloporphyrin containing chloro- or aminosilane, etc. This may also include electrostatically binding metals as by adsorption of cationic porphyrins like tetra(N-methyl-4-pyridyl)porphyrin on negatively charged porous materials in an alkaline environment, adsorption of anionic porphyrins/phthalocyanines on cationic porous materials such as trimethyl propyl ammonio-functionalized materials, etc.

The metal may be incorporated into the catalyst by adsorbing it as an aqueous cation, with or without simple ligands such as acetate. The metal may also be incorporated by adsorbing it as a volatile low-valent metal carbonyl, with or without post-treatment to decarbonylate the adsorbed metal carbonyl in-situ.

Methods for attaching metals to porous materials, and attaching functional groups to porous materials to which metals may thereto be attached, are known in the art, being described for example in U.S. Pat. No. 5,145,816, issued Sep. 8, 1992 to Beck et al., and in “A New Family of Mesoporous Molecular Sieves Prepared with Liquid Crystal Templates”, by Beck et al., J. Am. Chem. Soc., Vol. 114, No. 27, pp. 10834–10843 (1992), incorporated by reference herein in their entirety.


Preferred large more size redox catalysts useful herein have mean pore size of about 13 Angstroms or greater, more preferably of about 20–200 Angstroms, and most preferably about 30–100 Angstroms.

Also preferred redox catalysts herein have surface area of at least about 300 m²/g, more preferably at least about 400 m²/g and most preferably being at least about 500 m²/g.

Preferred large pore size redox catalysts are silicate or aluminosilicate redox catalyst materials. These include liquid crystal template synthesized silicate and aluminosilicate materials, such as those described in “A New Family of Mesoporous Molecular Sieves Prepared with Liquid Crystal Templates”, by Beck et al., J. Am. Chem. Soc., Vol. 114, No. 27, pp. 10834–10843 (1992). These materials are additionally characterized by high crystallinity and low water solubility. Pillared montmorillonites and similar pillared clays are preferably excluded. Most preferred are such materials which are crystalline on the basis of X-ray powder pattern.

Methods for evaluating the physical characteristics of the catalysts useful herein are well known in the art, being described for example in Kirk-Ohmer Encyclopedia of Chemical Technology, Fourth Edition, Vol. 5, pp. 383–418 (1993), the disclosures therein being incorporated herein by reference in their entirety.

Highly preferred are those catalysts described as “mesoporous molecular sieve” materials as taught, for example, in U.S. Pat. No. 5,102,643, issued Apr. 7, 1992 to Kresge et al., U.S. Pat. No. 5,250,282, issued Oct. 5, 1993 to Kresge et al., U.S. Pat. No. 5,264,203, issued Nov. 30, 1993 to Beck et al., U.S. Pat. No. 5,145,816, issued Sep. 8, 1992 to Beck et al., and U.S. Pat. No. 5,098,684, issued Mar. 24, 1992 to Kresge et al., the disclosures of all these patents being incorporated herein by reference in their entirety.

Preferred metals for use in these catalysts are manganese, nickel, chromium, copper, tungsten, titanium, cobalt, molybdenum, rhenium, and iron. The oxidative state of the metal is selected as desired by the formulator, for example manganese in the +0, +2, +3, +4, +5 state, iron in the 0, +2, +3, +4, +5 state, etc. The oxidative state of the large pore size redox catalyst may change during use consistent with its nature as a redox material.

While not intending to be limited by theory, it is believed that the present invention compositions provide dye transfer inhibition benefits by being able, due to the large pore size, to “capture” fugitive dyes and bring them into contact with the metal in these catalysts. Likewise, in bleach-containing compositions these catalysts can interact with the peracid material (e.g., hydrogen peroxide and/or bleach activator materials) to catalyze the bleach process without permitting an unacceptable fraction of the incorporated metal of the large pore size redox catalyst to come into contact with the fabric or surface being bleached, thereby reducing the chance for the catalyst to cause the damage typically seen with heretofore described bleach catalyst-containing detergents. Furthermore, a non-limiting theory is that these catalysts are useful with enzymes since enzyme-deactivating contact between the enzyme and the catalytic metal is reduced or eliminated.

Various other optional adjunct ingredients may also be used in combination with the large pore size redox catalysts herein to provide fully-formulated detergent compositions. The following ingredients are described for the convenience of the formulator, but are not intended to be limiting thereof.

Detertive Surfactants—Nonlimiting examples of surfactants useful herein typically at levels from about 1% to about 55%, by weight, include the conventional C<sub>12</sub>–C<sub>18</sub> alkyl benzene sulfonates ("LAS") and primary, branched-chain and random C<sub>10</sub>–C<sub>20</sub> alkyl sulfates ("AS"), the C<sub>8</sub>–C<sub>18</sub> secondary (7,3) alkyld sulfates of the formula CH<sub>2</sub>(CH<sub>2</sub>)<sub>6</sub>(CH<sub>3</sub>)<sub>2</sub>(CHOSO₃⁻)M⁺ CH₂ and CH₃(CH₂)₃(CHOSO₃⁻)M⁺ where x and y (x=1) are integers of at least about 7, preferably at least about 9, and M is a water-solubilizing cation, especially sodium, unsaturated sulfates such as oleyl sulfate, the C<sub>10</sub>–C<sub>16</sub> alkyl alkoxy sulfates ("AE₅S"; especially x up to about 7 EO ethoxy sulfates), C<sub>10</sub>–C<sub>16</sub> alkyl alkoxy carboxylates (especially the EO 1–5 ethoxyethoxyethoxylates), the C<sub>10</sub>–C<sub>18</sub> glycerol ethers, the C<sub>10</sub>–C<sub>18</sub> polyglycosides and their corresponding sulfated polyglycosides, and C<sub>12</sub>–C<sub>18</sub> alpha-sulfonated fatty acid esters. If desired, the conventional nonionic and amphoteric surfactants such as the C<sub>12</sub>–C<sub>18</sub> alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxyethoxides and C<sub>10</sub>–C<sub>12</sub> alkyl phenol alkoxylates (especially ethoxylates and mixed ethoxypropoxy), C<sub>12</sub>–C<sub>18</sub> betaaines and sulfobetaines ("sultaines"), C<sub>6</sub>–C<sub>18</sub> amine oxides, sarcosinates such as oleyl sarcosinate, and the like can also be included in the overall compositions. The C<sub>10</sub>–C<sub>18</sub> N-alkyl polyhydroxy fatty acid amides can also be used. Typical
examples include the C₁₂₋₁₈ N-methylglucamides. See WO 9,206,154. Other sugar-derived surfactants include the N-alkoxy polyhydroy fatty acid amides, such as C₁₀₋₁₈ N-(3-methoxypropyl) gluamicide. The N-propyl through N-ethyl C₁₂₋₁₈ gluamicides can be used for low sudsing. C₁₀₋₀₂₂ conventional soaps may also be used. If high sudsing is desired, the branched-chain C₁₀₋₁₆ soaps may be used. Mixtures of anionic and nonionic surfactants are especially useful. Other conventional useful surfactants are listed in standard texts.

Builders—Detergent builders can optionally be included in the compositions herein to assist in controlling mineral hardness. Inorganic as well as organic builders can be used. Builders are typically used in fabric laundering compositions to assist in the removal of particulate soils.

The level of builder can vary widely depending upon the end use of the composition and its desired physical form. When present, the compositions will typically comprise at least about 1% builder, preferably from about 1% to about 80%. Liquid formulations typically comprise from about 5% to about 50%, more typically about 5% to about 40% by weight, of detergent builder. Granular formulations typically comprise from about 1% to about 80%, more typically from about 5% to about 50% by weight, of the detergent builder. Lower or higher levels of builder, however, are not meant to be excluded.

Inorganic or P-containing detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric metaphosphates), phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulfates, and aluminosilicates. However, non-phosphate builders are required in some locales. Importantly, the compositions herein function surprisingly well even in the presence of the so-called “weak” builders (as compared with phosphates) such as citrate, or in the so-called “underbuilt” situation that may occur with zeolite or layered silicate builders.

Examples of silicate builders are the alkali metal silicates, particularly those having a SiO₂:N₂₃ ratio in the range 1.0:1 to 3.2:1 and layered silicates, such as the layered sodium silicates described in U.S. Pat. No. 4,664,839, issued May 12, 1987 to H. P. Rieck. NaSKS-6 is the trademark for a crystalline layered silicate marketed by Hoechst (commonly abbreviated herein as “SKS-6”). Unlike zeolite builders, the Na SKS-6 silicate builder does not contain aluminate. NaSKS-6 has the delta-Na₂SO₄ morphology form of layered silicate. It can be prepared by methods such as those described in German DE-A-3,417,649 and DE-A-3,742,043. SKS-6 is a highly preferred layered silicate for use herein, but other such layered silicates, such as those having the general formula Na₃MₓSi₃O₁ₓ₊¹H₂O wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 to 10, may be used herein. Various other layered silicates from Hoechst include NaSKS-5, NaSKS-7 and NaSKS-11, as the alpha, beta and gamma forms. As noted above, the delta-Na₂SO₄ (NaSKs-6 form) is most preferred for use herein. Other silicates may also be useful such as for example magnesium silicate, which can serve as a crisping agent in granular formulations, as a stabilizing agent for oxygen bleaches, and as a component of sud control systems.

Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001, published on Nov. 15, 1973.

Aluminosilicate builders are useful in the present invention. Aluminosilicate builders are of great importance in most currently marketed heavy duty granular detergent compositions, and can also be a significant builder ingredient in liquid detergent formulations. Aluminosilicate builders include those having the empirical formula:

\[ Mₓ(Al₂O₃)(SiO₂)₃·xH₂O \]

wherein x, y and z are integers usually of at least 6, the molar ratio of z to y is in the range from 1.0 to 6, and x is an integer from 0 to about 264, and M is a Group IA or IIA element, e.g., Na, K, Mg, Ca with valence n.

Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystal-line or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Pat. No. 3,985,669, Krummel et al., issued Oct. 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:

\[ Naₓ(Al₂O₃)(SiO₂)₃·xH₂O \]

wherein x is from about 20 to about 30, especially about 27. This material is known as Zeolite A. Dehydrated zeolites (x=0–10) may also be used herein. Preferably, the aluminosilicate has a particle size of about 0.1–10 microns in diameter.

Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polyacrylate compounds. As used herein, “polyacrylate” refers to compounds having a plurality of carboxylate groups, preferably at least 3 carboxylates. Polyacrylate builder can generally be added to the composition in acid form, but can also be added in the form of a neutralized salt. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred.

Included among the polyacrylate builders are a variety of categories of useful materials. One important category of polyacrylate builders encompasses the other polyacrylates, including oxysuccinate, as disclosed in Berg, U.S. Pat. No. 3,128,287, issued Apr. 7, 1964, and Lambert, et al., U.S. Pat. No. 3,635,830, issued Jan. 18, 1972. See also “TMS/TDS” builders of U.S. Pat. No. 4,663,071, issued to Bush et al., on May 5, 1987. Suitable ether polyacrylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Pat. Nos. 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

Other useful detergency builders include the other hydroxypropylocarbonylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulfonic acid, and carboxymethylxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitritriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxysuccinic acid, polyacetic acid, benzene 1,3,5-tricarboxylic acid, carboxymethylxysuccinic acid, and soluble salts thereof.

Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of particular importance for heavy duty liquid detergent formulations due to their availability from renewable resources and their biodegradability. Citrates can also be used in...
granular compositions, especially in combination with zeo-
lite and/or layered silicate builders. Oxydisuccinates are also
especially useful in such compositions and combinations.

Also suitable in the detergent compositions of the present
invention are the 3,3-dicarboxy-4-oxa-1,6-hexamethio-
ates and the related compounds disclosed in U.S. Pat. No.
4,566,984, Bush, issued Jan. 28, 1986. Useful succinic acid
builders include the C\textsubscript{6}-C\textsubscript{12} alkyI and alkyl succinic acids
and salts thereof. A particularly preferred compound of this
type is dodecensuccinic acid. Specific examples of succi-
nate builders include: laurylsuccinate, myristylsuccinate,
palmitylsuccinate, 2-dodecensuccinate (preferred), 2-pen-
tadecensuccinate, and the like. Laurylsuccinates are the
preferred builders of this group, and are described in
European Patent Application 86200690.5/200,263, published
Nov. 5, 1986.

Other suitable polycarboxylates are disclosed in U.S. Pat.
No. 4,144,226, Crutchfield et al., issued Mar. 13, 1979 and
in U.S. Pat. No. 3,308,067, Diehl, issued Mar. 7, 1967. See also
Diehl U.S. Pat. No. 3,723,322.

Fatty acids, e.g., C\textsubscript{16}-C\textsubscript{18} monooacyl cyclic acids such as
oleic acid and/or its salts, can also be incorporated into the
compositions alone, or in combination with the aforesaid
builders, especially citrate and/or the succinate builders, to
provide additional builder activity. Such use of fatty acids
will generally result in a diminution of sudsing, which
should be taken into account by the formulator.

In situations where phosphonate-based builders can be
used, and especially in the formulation of bars used for
hand-lathering operations, the various alkali metal phos-
phates such as the well-known sodium tripolyphosphates,
sodium pyrophosphate and sodium orthophosphate can be
used. Phosphonate builders such as ethane-1-hydroxy-1,1-
diphosphonate and other known phosphonates (see, for
example, U.S. Pat. Nos. 3,159,581; 3,213,030; 3,422,021;
3,400,148 and 3,422,137) can also be used.

Enzymes—Enzymes may be included in the formulations
herein for a wide variety of fabric laundering purposes,
including removal of protein-based, carbohydrate-based,
or triglyceride-based stains, for example, and for the preven-
tion of refugee dye transfer, and for fabric restoration.

The enzymes to be incorporated include proteases, amylases,
lipases, cellulases, and peroxidases, as well as mixtures
thereof. Other types of enzymes may also be included.

They may be of any suitable origin, such as vegetable, animal,
bacterial, fungal and yeast origin. However, their choice is
governed by several factors such as pH-activity and/or
stability profile, thermostability, stability versus active
detergents, builders and so on. In this respect bacterial or
fungal enzymes are preferred, such as bacterial amylases and
proteases, and fungal cellulases.

Enzymes are normally incorporated at levels sufficient to
provide up to about 5 mg by weight, more typically about
0.001 mg to about 3 mg, of active enzyme per gram of the
composition. Stated otherwise, the compositions herein
will typically comprise from about 0.001% to about 5%, prefer-
ably 0.01%–2% by weight of a commercial enzyme prepara-
tion. Protease enzymes are usually present in such com-
mercial preparations at levels sufficient to provide from
0.005 to 0.1 Anson units (AU) of activity per gram of
composition.

Suitable examples of proteases are the subtilisins which
are obtained from particular strains of B. subtilis and B.
licheniforms. Another suitable protease is obtained from a
strain of Bacillus, having maximum activity throughout the
pH range of 8–12, developed and sold by Novo Industries
A/S under the registered trade name ESPERASE. The
preparation of this enzyme and analogous enzymes is
described in British Patent Specification No. 1,243,784 of
Novo. Proteolytic enzymes suitable for removing protein-
based stains that are commercially available include those
sold under the tradenames ALCALASE and SAVINASE by
Novo Industries A/S (Denmark) and MAXATASE by Inter-
national Bio-Synthetics, Inc. (The Netherlands). Other pro-
teases include Protease A (see European Patent Application
130,756, published Jan. 9, 1985) and Protease B (see Euro-
pean Patent Application Serial No. 87303761.8, filed Apr.
28, 1987, and European Patent Application 130,756, Bott et
al., published Jan. 9, 1985). Other proteases include Protease
9, 1985) and Protease B (see European Patent Application
Serial No. 87303761.8, filed Apr. 28, 1987, and European
Patent Application 130,756, Bott et al., published Jan. 9,
1985). Other proteases include Protease A (see European
Patent Application 130,756, published Jan. 9, 1985) and
Protease B (see European Patent Application Serial No.
87303761.8, filed Apr. 28, 1987, and European Patent
Application 130,756, Bott et al., published Jan. 9, 1985).

Most preferred is what is called herein "Protease C", which is
a variant of an alkaline serine protease from Bacillus, particu-
larly Bacillus luteus, in which arginine replaced lysine at
position 27, tyrosine replaced valine at position 104, serine
replaced asparagine at position 123, and alanine replaced
threonine at position 274. Protease C is described in EP
09915958.4; U.S. Pat. No. 5,181,250; and U.S. Pat.
No. 5,204,015. Also especially preferred are protease which
are described in copending application U.S. Ser. No. 08/136,
797, entitled Protease-containing Cleaning Compositions
and copending application U.S. Ser. No. 08/136,626,
entitled Bleaching Compositions Comprising Protease
Enzymes, which are incorporated herein by reference.

Genetically modified variants, particularly of Protease C,
are also included herein.

Amylases include, for example, a-amylases described in
British Patent Specification No. 1,296,839 (Novo), RAPID-
ASE, International Bio-Synthetics, Inc. and TERR-
MAMYL, Novo Industries.

The cellulase usable in the present invention include both
bacterial or fungal cellulase. Preferably, they will have a pH
optimum of between 5 and 9.5. Suitable cellulases are
disclosed in U.S. Pat. No. 4,435,307, Barbesgaard et al.,
issued Mar. 6, 1984, which discloses fungal cellulase pro-
duced from Humicola insolens and Humicola strain
DSM1800 or a cellulase 212-producing fungus belonging to
the genus Aeromonas, and cellulase extracted from the
hepatopancreas of a marine mollusk (Dolabella auricula
Solander), suitable cellulases are also disclosed in GB-
A-2075.028; GB-A-209.275 and DE-OS-2.247.832. Cellu-
lases such as CAREZYM (Novo) are especially useful,
since they provide additional softening and appearance
benefits to fabrics laundered in the present compositions.

Suitable lipase enzymes for detergent usage include those
produced by microorganisms of the Pseudomonas group,
such as Pseudomonas stutzeri ATCC 19,154, as disclosed
in British Patent 1,372,034. See also lipases in Japanese Patent
Application 53/20487, laid open after preliminary inspection
in Feb. 24, 1978. This lipase is available from Amam Pharmaceutical
Co. Ltd., Nagoya, Japan, under the trade name Lipase
P “Amano,” hereinafter referred to as “Amano-P” Other
commercial lipases include Amano-CES, lipases ex Chro-
mobacter viscosum, e.g. Chromobacter viscosum var. lipoly-
ticus NRRLB 3673, commercially available from Toyo
Jozo Co., Tanata, Japan; and further Chromobacter viscosum
lipases from U.S. Biochemical Corp., U.S.A. and Disoynt
Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. The LIPO-LASE enzyme derived from *Humicola lanuginosa* and commercially available from Novo (see also EPO 341,947) is a preferred lipase for use herein.

Peroxidase enzymes are used in combination with oxygen sources, e.g., percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are used for "solution bleaching," i.e., to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase, and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813, published Oct. 19, 1989, by O. Kirk, assigned to Novo Industries A/S. It may be desired to use, in combination with these peroxidases, materials viewed as being peroxidase accelerators such as phenolsulfonate and/or phenodiazine, calcium or magnesium ions and materials for their incorporation into synthetic detergent compositions are also disclosed in U.S. Pat. No. 3,553,139, issued Jan. 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. Pat. No. 4,101,457, Place et al., issued Jul. 18, 1978, and in U.S. Pat. No. 4,507,219, Hughes, issued Mar. 26, 1985, both. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. Pat. No. 4,261,868, Hora et al, issued Apr. 14, 1981.

Enzyme Stabilizers—A preferred optional ingredient for use in the present compositions which comprise enzymes is enzyme stabilizers. Enzymes for use in detergents can be stabilized by various techniques. Enzyme stabilization techniques are disclosed and exemplified in U.S. Pat. No. 3,600,319, issued Aug. 17, 1971 to Godec, et al., and in European Patent Application Publication No. 0 199 405, Application No. 86200586.5, published Oct. 29, 1986, Venable et al., Enzyme stabilization systems are also described, for example, in U.S. Pat. No. 3,519,570. The enzymes employed herein can be stabilized by the presence of water-soluble sources of calcium and/or magnesium ions in the finished compositions which provide such ions to the enzymes. (Calcium ions are generally somewhat more effective than magnesium ions and are preferred herein if only one type of cation is being used.) Additional stability can be provided by the presence of various other art-disclosed stabilizers, especially borate species: see Severson, U.S. Pat. No. 4,537,706. Typical detergents, especially liquids, will comprise from about 1 to about 30, preferably from about 2 to about 20, more preferably from about 5 to about 15, and most preferably from about 8 to about 12, millimoles of calcium ion per liter of finished composition. This can vary somewhat, depending on the amount of enzyme present and its response to the calcium ion, or magnesium ions. The level of calcium or magnesium ions should be selected so that there is always some minimum level available for the enzyme, after allowing for complexation with builders, fatty acids, etc., in the composition. Any water-soluble calcium or magnesium salt can be used as the source of calcium or magnesium ions, including, but not limited to, calcium chloride, calcium sulfate, calcium malate, calcium maleate, calcium hydroxide, calcium formate, and calcium acetate, and the corresponding magnesium salts. A small amount of calcium ion, generally from about 0.05 to about 0.4 millimoles per liter, is often also present in the composition due to calcium in the enzyme slurry and formula water. In solid detergent compositions the formulation may include a sufficient quantity of a water-soluble calcium ion source to provide such amounts in the laundry liquor. In the alternative, natural water hardness may suffice.

It is to be understood that the foregoing levels of calcium and/or magnesium ions are sufficient to provide enzyme stability. More calcium and/or magnesium ions can be added to the compositions to provide an additional measure of grease removal performance. Accordingly, as a general proposition the compositions herein will typically comprise about 0.05% to about 2% by weight of a water-soluble source of calcium or magnesium ions, or both. The amount can vary, of course, with the amount and type of enzyme employed in the composition.

The compositions herein may also optionally, but preferably, contain various additional stabilizers, especially borate-type stabilizers. Typically, such stabilizers will be used at levels in the compositions from about 0.25% to about 10%, preferably from about 0.5% to about 5%, more preferably from about 0.75% to about 3%, by weight of boric acid or other borate compound capable of forming boric acid in the composition encountered on the bauxitic alicyclic acid bleach.

Boric acid is preferred, although other compounds such as borax oxide, borax and other alkali metal borates (e.g., sodium ortho-, meta- and pyroborate, and sodium pentaborate) are suitable. Substituted boric acids (e.g., phenylboronic acid, butane boronic acid, and p-bromo phenylboronic acid) can also be used in place of boric acid. It is to be recognized that such materials may also be used in formulations as the sole stabilizer as well as being used in combination with added calcium and/or magnesium ions.

Finally, it may be desired to add chlorine scavengers, especially to process-containing compositions, to protect the enzymes from chlorine typically present in municipal water supplies. Such materials are described, for example, in U.S. Pat. No. 4,810,413 to Pancheri et al.

Bleaching Compounds—Bleaching Agents and Bleach Activators—The detergent compositions herein may optionally, but preferably, contain bleaching agents or bleaching compositions containing a bleaching agent and one or more bleach activators. When present, bleaching agents will typically be at levels of from about 1% to about 30%, more typically from about 5% to about 20%, of the detergent composition, especially for home laundering. If present, the amount of bleach activators will typically be from about 0.1% to about 60%, more typically from about 0.5% to about 40% of the bleaching composition comprising the bleaching agent-plus-bleach activator.

The bleaching agents used herein can be any of the bleaching agents useful for detergent compositions in textile cleaning or other cleaning purposes that are now known or become known. These include oxygen bleaches as well as other bleaching agents. Perborate bleaches, e.g., sodium perborate (e.g., mono- or tetra-hydrate) can be used herein.

Another category of bleaching agent that can be used without restriction encompasses peroxycarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include monoper oxyphthalate hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-nonylaminoo-4-oxoperoxybutyric acid and diperoxycanedioic acid. Such bleaching agents are disclosed in U.S. Pat. No. 4,483,781, Hartman, issued Nov. 20, 1984, U.S. patent application Ser. No. 704,446, Burns et al, filed Jun. 3, 1985, European Patent Application 0,133,354, Banks et al, published Feb. 20, 1985, and U.S. Pat. No. 4,412,934, Chung et al, issued Nov. 1, 1983. Highly preferred bleaching agents also include 6-nonylamino-6-oxoper oxyacrylic acid as described in U.S. Pat. No. 4,634,571, issued Jan. 6, 1987 to Burns et al.
Peroxygen bleaching agents can also be used. Suitable peroxygen bleaching compounds include sodium carbonate peroxidehydride and equivalent "percarbon" bleaches, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxyde. Persulfate bleach (e.g., OXONE, manufactured commercially by DuPont) can also be used.

A preferred percarbonate bleach comprises dry particles having an average particle size in the range from about 500 micrometers to about 1,000 micrometers, not more than about 10% by weight of said particles being smaller than about 200 micrometers and not more than about 10% by weight of said particles being larger than about 1,250 micrometers. Optionally, the percarbonate can be coated with silicate, borate or water-soluble surfactants. Percarbonate is available from various commercial sources such as FMC, Solvay and Tokai Denka.

Mixtures of bleaching agents can also be used.

Peroxygen bleaching agents, the perborates, the percarbonates, etc., are preferably combined with bleach activators, which lead to the in situ production in aqueous solution (i.e., during the washing process) of the peroxy acid corresponding to the bleach activator. Various nonlimiting examples of activators are disclosed in U.S. Pat. No. 4,915,854, issued Apr. 10, 1990 to Mao et al., and U.S. Pat. No. 4,412,934. The nonanoyloxybenzene sulfonate (NOBS) and tetraacetylethylene diamine (TAED) activators are typical, and mixtures thereof can also be used. See also U.S. Pat. No. 4,634,551 for other typical bleaches and activators useful herein.

Highly preferred amido-derived bleach activators are those of the formula:

$$R^1N^2(C(=O)NR^3)^x(O)C(=O)R^4$$

wherein $R^1$ is an alkyl group containing from about 6 to about 12 carbon atoms, $R^2$ is an alkylene containing from 1 to about 6 carbon atoms, $R^3$ is $H$ or alkyl, aryl, or alkyaryl containing from about 1 to about 10 carbon atoms, and $L$ is any suitable leaving group. A leaving group is any group that is displaced from the bleach activator as a consequence of the nucleophilic attack on the bleach activator by the hydrolysis anion. A preferred leaving group is phenyl sulfonate.

Preferred examples of bleach activators of the above formulae include (6-octanamido-caproyl)oxybenzenesulfonate, (6-nonanamido-caproyl)oxybenzenesulfonate, (6-decanamido-caproyl)oxybenzenesulfonate, and mixtures thereof as described in U.S. Pat. No. 4,634,551, incorporated herein by reference.

Another class of bleach activators comprises the benzoxazin-type activators disclosed by Hodges et al in U.S. Pat. No. 4,966,723, issued Oct. 30, 1990, incorporated herein by reference. A highly preferred activator of the benzoxazin-type is:

Still another class of preferred bleach activators includes the acyl lactam activators, especially acyl caprolactams and acyl valerolactams of the formulae:

$$R^5C(=O)NR^6C(=O)NR^7C(=O)R^8$$

wherein $R^8$ is an alkyl, aryl, alkoxyaryl, or alkaryl group containing from 1 to about 12 carbon atoms. Highly preferred lactam activators include benzoyl caprolactam, octanoyl caprolactam, 3,5,5-trimethylhexanoyl caprolactam, nonanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, benzoyl valerolactam, octanoyl valerolactam, decanoyl valerolactam, undecanoyl valerolactam, 3,5,5-trimethylhexanoyl valerolactam and mixtures thereof. See also U.S. Pat. No. 4,545,784, issued to Sanderson, Oct. 8, 1985, incorporated herein by reference, which discloses acyl caprolactams, including benzoyl caprolactam, adsorbed into sodium perborate.

Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines. See U.S. Pat. No. 4,033,718, issued Jul. 5, 1977 to Holcombe et al. If used, detergent compositions will typically contain from about 0.025% to about 1.25%, by weight, of such bleaches, especially sulfonated zinc phthalocyanine.

If desired, the present compositions may also be catalyzed by means of art known manganese compound. Such compounds are well known in the art and include, for example, the manganese-based catalysts disclosed in U.S. Pat. No. 5,246,621, U.S. Pat. No. 5,244,594; U.S. Pat. No. 5,194,416; U.S. Pat. No. 5,114,606; and European Pat. App. Pub. Nos. 549,271 A1, 549,272 A1, 544,404A2, and 544,490A1: Preferred examples of these catalysts include MnO($u$-(O)-(1,4,7-triazacyclononane)(PF$_6$)$_2$, Mn$_x$O($u$-(O)-(1,4,7-triazacyclononane)(PF$_6$)$_2$, Mn$^{III}$($u$-(O)-(1,4,7-triazacyclononane)(PF$_6$)$_2$, Mn$^{IV}$($u$-(O)-(1,4,7-triazacyclononane)(PF$_6$)$_2$, Mn$^{III}$($u$-(O)-(1,4,7-triazacyclononane)(PF$_6$)$_2$, Mn$^{IV}$($u$-(O)-(1,4,7-triazacyclononane)(PF$_6$)$_2$, Mn$^{IV}$-$u$-(O)-(1,4,7-triazacyclononane)(PF$_6$)$_2$, and mixtures thereof. Other metal-based bleach catalysts include those disclosed in U.S. Pat. No. 4,430,243 and U.S. Pat. No. 5,114,611. The use of manganese with various complex ligands to enhance bleaching is also reported in the following U.S. Pat. Nos.: 4,728,455; 5,284,944; 5,246,612; 5,256,779; 5,280,117; 5,274,147; 5,153,161; and 5,227,084.

Polymeric Soil Release Agent—Any polymeric soil release agent known to those skilled in the art can optionally be employed in the compositions and processes of this invention. Polymeric soil release agents are characterized by having both hydrophilic segments, to hydrophilize the surface of hydrophobic fibers, such as polyester and nylon, and hydrophobic segments, to deposit upon hydrophobic fibers and remain adhered thereto through completion of washing and rinsing cycles and, thus, serve as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with the soil release agent to be more easily cleaned in later washing procedures.

The polymeric soil release agents useful herein especially include those soil release agents having: (a) one or more nonionic hydrophilic components consisting essentially of (i) polyoxyethylene segments with a degree of polymerization of at least 2, or (ii) oxypropylene or polyoxypropylene segments with a degree of polymerization of from 2 to 10, wherein said hydrophile segment does not encompass any
oxypolypropylene unit unless it is bonded to adjacent moieties at each end by ether linkages, or (iii) a mixture of oxalkylene units comprising oxylene and from 1 to about 30 oxypolyoxylene units wherein said mixture contains a sufficient amount of oxylene units such that the hydrophilic component has hydrophilicity great enough to increase the hydrophilicity of conventional polyester synthetic fiber surfaces upon deposit of the soil release agent on such surface, said hydrophile segments preferably comprising at least about 25% oxylene units and more preferably, especially for such components having about 20 to 30 oxypolypropylene units, at least about 50% oxylene units; or (b) one or more hydrophobe components comprising (i) C₃ oxalkylene terpethalate segments, wherein, if said hydrophobe components also comprise oxylene terpethalate, the ratio of oxylene terpethalate:C₃ oxalkylene terpethalate is about 2:1 or lower, (ii) C₂₋C₅ alkylene or ox C₂₋C₅ alkylene segments, or mixtures therein, (iii) poly (vinyl ester) segments, preferably polyvinyl acetate, having a degree of polymerization of at least 2, or (iv) C₁₋C₅ alkyl ether or C₂ hydroxyalkyl ether substituents, or mixtures therein, wherein said substituents are present in the form of C₅₋C₉ alkyl ether or C₅ hydroxyalkyl ether cellulose derivatives, or mixtures therein, and such cellulose derivatives are amphiphilic, whereby they have a sufficient level of C₁₋C₅ alkyl ether and/or C₅ hydroxyalkyl ether units to deposit upon conventional polyester synthetic fiber surfaces and retain a sufficient level of hydroxyls, once adhered to such conventional synthetic fiber surface, to increase fiber surface hydrophilicity, or a combination of (a) and (b). Typically, the oxylene segments of (a)(i) will have a degree of polymerization of from about 200, although higher levels can be used, preferably from 3 to about 150, more preferably from 6 to about 100. Suitable oxylene C₂₋C₅ alkylene hydrophobe segments include, but are not limited to, end-caps of polymeric soil release agents such as MO₃S(CH₂)₄OCH₂CH₂O—, where M is sodium and n is an integer from 4–6, as disclosed in U.S. Pat. No. 4,721,580, issued Jan. 26, 1988 to Gosselink.

Polymeric soil release agents useful in the present invention also include cellulose derivatives such as hydroxyether cellulose polymers, copolymeric blocks of ethylene terephthalate or propylene terepethalate with oxylene oxide or polypropylene oxide terpethalate, and the like. Such agents are commercially available and include hydroxylethers of cellulose such as METHOCEL (Dow). Cellulosic soil release agents for use herein also include those selected from the group consisting of C₂₋C₅ alkyl and C₆ hydroxyalkyl cellulose; see U.S. Pat. No. 4,000,093, issued Dec. 28, 1976 to Nicol, et al.

Soil release agents characterized by poly(vinyl ester) hydrophobe segments include graft copolymers of poly(vinyl ester), e.g., C₃₋C₅ vinyl esters, preferably poly(vinyl acetate) grafted onto polyalkylene oxide backbones, such as polyethylene oxide backbone. See European Patent Application 0 219 048, published Apr. 22, 1987 by Kud, et al.

Commercially available soil release agents of this kind include the SOKALAN type of material, e.g., SOKALAN HP-22, available from BASF (West Germany).

One type of preferred soil release agent is a copolymer having random blocks of ethylene terepethalate and polyethylene oxide (PEO) terepethalate. The molecular weight of this polymeric soil release agent is in the range of from about 25,000 to about 55,000. See U.S. Pat. No. 3,599,230 to Hays, issued May 25, 1971 and U.S. Pat. No. 3,893,929 to Badger (issued Jul. 8, 1975).

Another preferred polymeric soil release agent is a polyester with repeat units of ethylene terpethalate units containing 10–15% by weight of ethylene terepethalate units together with 90–80% by weight of polyoxyethylene terepethalate units, derived from a polyoxyethylene glycol of average molecular weight 300–5,000. Examples of this polymer include the commercially available material ZEL-CON 5126 (from Dupont) and MILLSEAL T (from ICI). See also U.S. Pat. No. 4,702,857, issued Oct. 27, 1987 to Gosselink.

Another preferred polymeric soil release agent is a sulfonated product of a substantially linear ester oligomer comprised of an oligomeric ester backbone of terephthaloyl and oxalkyleneoxy repeat units and terminal moieties covalently attached to the backbone. These soil release agents are described fully in U.S. Pat. No. 4,968,451, issued Nov. 6, 1990 to J. J. Scheibel and E. P. Gosselink. Other suitable polymeric soil release agents include the terepethalate polymers of U.S. Pat. No. 4,711,730, issued Dec. 8, 1987 to Gosselink et al., the anionic end-capped oligomeric esters of U.S. Pat. No. 4,721,580, issued Jan. 26, 1988 to Gosselink, and terepethalate oligomer components of U.S. Pat. No. 4,702,857, issued Oct. 27, 1987 to Gosselink.

Preferred polymeric soil release agents also include the soil release agents of U.S. Pat. No. 4,877,896, issued Oct. 31, 1989 to Maldonado et al., which discloses anionic, especially sulfonaryl, end-capped terepethalate esters.

Still another preferred soil release agent is an oligomer with repeat units of terephthaloyl units, sulfosopropylterephthaloyl units, oxetylenoxylene and oxo-1,2-propylene units. The repeat units form the backbone of the oligomer and are preferably terminated with modified isocyanate end-caps. A particularly preferred soil release agent of this type comprises about one sulfoxopropylolyl unit, 5 terepethaloyl units, oxetylenoxylene and oxo-1,2-propyleneoxy units in a ratio of from about 1.7 to about 1.8, and two end-caps units of sodium 2-(2-hydroxyethoxy)ethanesulfonate. Said soil release agent also comprises from about 0.5% to about 20%, by weight of the oligomer, of a crystalline-reducing stabilizer, preferably selected from the group consisting of xylene sulfonate, cumene sulfonate, toluene sulfonate, and mixtures thereof.

If utilized, soil release agents will generally comprise from about 0.01% to about 10.0%, by weight, of the detergent compositions herein, typically from about 0.1% to about 5%, preferably from about 0.2% to about 3.0%.

Dye Transfer Inhibiting Agents—The compositions of the present invention may also include one or more materials effective for inhibiting the transfer of dyes from one fabric to another during the cleaning process. Generally, such dye transfer inhibiting agents include polyvinyl pyrrolidone polymers, polyanime N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, manganese phthalocyanine, peroxidases, and mixtures thereof. If used, these agents typically comprise from about 0.01% to about 10% by weight of the composition, preferably from about 0.01% to about 5%, and more preferably from about 0.05% to about 2%.

More specifically, the polyanime N-oxide polymers preferred for use herein contain units having the following structural formula: R—A—P; wherein P is a polymerizable unit to which an N—O group can be attached or the N—O group can form part of the polymerizable unit or the N—O group can be attached to both units; A is one of the following structures: —NC(O)—, —C(O)O—, —S—, —O—, —N=; x is 0 or 1; and R is alphabetic, ethoxylated alphatics, aromatics, heterocyclic or alicyclic groups or any combination thereof to which the nitrogen of the N—O group can be attached or the N—O group is part of these groups. Preferred
polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine and derivatives thereof.

The N—O group can be represented by the following general structures:

\[
\begin{align*}
\text{N—O} & \quad \text{N—O} \\
(R_3) & \quad (R_3)
\end{align*}
\]

wherein \( R_1, R_2, R_3 \) are aliphatic, aromatic, heterocyclic or alicyclic groups or combinations thereof, x, y and z are 0 or 1; and the nitrogen of the N—O group can be attached or form part of any of the aforementioned groups. The amine oxide unit of the polyamine N-oxides has a pK\text{a} < 10, preferably pK\text{a} > 7, more preferably pK\text{a} > 6.

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers, polyamide, polynitriles, polyacrylates and mixtures thereof. These polymers include random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is an N-oxide. The amine N-oxide polymers typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1,000,000. However, the number of amine N-oxide groups present in the polyamine oxide polymer can be varied by appropriate copolymerization by an appropriate degree of N-oxidation. The polyamine oxides can be obtained in almost any degree of polymerization. Typically, the average molecular weight is within the range of 500 to 1,000,000; more preferably 1,000 to 500,000; most preferably 5,000 to 100,000. This preferred class of materials can be referred to as "PVNO".

The most preferred polyamine N-oxide useful in the detergent compositions herein is poly(4-vinylpyridine-N-oxide) which as an average molecular weight of about 50,000 and an amine to amine N-oxide ratio of about 1:4. Copolymers of N-vinylpyrrolidone and N-vinylidimaleate polymers (referred to as a class as "PVPVI") are also preferred for use herein. Preferably the PVPVI has an average molecular weight range from 5,000 to 1,000,000, more preferably from 5,000 to 200,000, and most preferably from 10,000 to 20,000. (The average molecular weight range is determined by light scattering as described in Barth, et al., Chemical Analysis, Vol 113, "Modern Methods of Polymer Characterization", the disclosures of which are incorporated herein by reference.) The PVPVI copolymers typically have a molar ratio of N-vinylidimaleate to N-vinylpyrrolidone from 1:1 to 0.2:1, more preferably from 0.8:1 to 0.3:1, most preferably from 0.6:1 to 0.4:1. These copolymers can be either linear or branched.

The present invention compositions also may employ a polyvinylpyrrolidone ("PVP") having an average molecular weight of from about 5,000 to about 400,000, preferably from about 5,000 to about 200,000, and more preferably from about 5,000 to about 50,000. PVP's are known to persons skilled in the detergent field; see, for example, EP-A-262,897 and EP-A-256,696, incorporated herein by reference. Compositions containing PVP can also contain polyethylene glycol ("PEG") having an average molecular weight from about 500 to about 100,000, preferably from about 1,000 to about 10,000. Preferably, the ratio of PEG to PVP on a ppm basis delivered in wash solutions is from about 2:1 to about 10:1, and more preferably from about 3:1 to about 10:1.

The detergent compositions herein may also optionally contain from about 0.005% to 5% by weight of certain types of hydrophilic optical brighteners which also provide a dye transfer inhibition action. If used, the compositions herein will preferably comprise from about 0.01% to 1% by weight of such optical brighteners.

The hydrophilic optical brighteners useful in the present invention are those having the structural formula:

\[
\begin{align*}
\text{R}_1 & \quad \text{N} \quad \text{R}_2 \\
\text{H} & \quad \text{C} \quad \text{C} \\
\text{R}_3 & \quad \text{N} \quad \text{H} \\
\text{SO}_2\text{M} & \quad \text{SO}_2\text{M}
\end{align*}
\]

wherein \( R_1, R_2, R_3 \) are selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl; \( R_3 \) is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino, morphilino, chloro and amino; and \( M \) is a salt forming cation such as sodium or potassium.

When in the above formula, \( R_1 \) is anilino, \( R_2 \) is N-2-bis-hydroxyethyl and \( M \) is a cation such as sodium, the brightener is 4,4',bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal-UNPA-GX by Ciba-Geigy Corporation. Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the detergent compositions herein.

When in the above formula, \( R_1 \) is anilino, \( R_2 \) is N-2-hydroxyethyl-N-2-methylamino and \( M \) is a cation such as sodium, the brightener is 4,4',bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal 5BM-GX by Ciba-Geigy Corporation.

When in the above formula, \( R_1 \) is anilino, \( R_2 \) is morphilino and \( M \) is a cation such as sodium, the brightener is 4,4',bis[(4-anilino-6-morphilino-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid, sodium salt. This particular brightener species is commercially marketed under the tradename Tinopal AMS-GX by Ciba-Geigy Corporation.

The specific optical brightener species selected for use in the present invention provide especially effective dye transfer inhibition performance benefits when used in combination with the selected polymeric dye transfer inhibiting agents hereinbefore described. The combination of such selected polymeric materials (e.g., PVNO and/or PVPVI) with such selected optical brighteners (e.g., Tinopal UNPA-GX, Tinopal 5BM-GX, Tinopal-PLC, and/or Tinopal AMS-GX) provides significantly better dye transfer inhibition in aqueous wash solutions than does either of these two detergent composition components when used alone. Without being bound by theory, it is believed that such brighteners work this way because they have high affinity for fabrics in the wash solution and therefore deposit relatively quickly on
these fabrics. The extent to which brighteners deposit on fabrics in the wash solution can be defined by a parameter called the "exhaustion coefficient". The exhaustion coefficient is in general as the ratio of a) the brightener material deposited on fabric to b) the initial brightener concentration in the wash liquor. Brighteners with relatively high exhaustion coefficients are the most suitable for inhibiting dye transfer in the context of the present invention.

Of course, it will be appreciated that other, conventional optical brightener types of compounds can optionally be used in the present compositions to provide conventional fabric "brightness" benefits, rather than a true dye transfer inhibiting effect. Such usage is conventional and well-known to detergent formulations.

Polymeric Dispersing Agents—Polymeric dispersing agents can advantageously be utilized at levels from about 0.1% to about 7%, by weight, in the compositions herein. Suitable polymeric dispersing agents include polymeric polycarboxylates and polyethylene glycols, although others may be preferred as well. Polymeric polycarboxylate materials can be prepared by polymerizing or copolymerizing suitable unsaturated monomers, preferably in their acid form. Unsaturated monomeric acids that can be polymerized to form suitable polymeric polycarboxylates include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylene malonic acid. The presence in the polymeric polycarboxylates herein or monomeric segments, containing no carboxylate radicals such as vinylmethyl ether, styrene, ethylene, etc. is suitable provided that such segments do not constitute more than about 40% by weight.

Particularly suitable polymeric polycarboxylates can be derived from acrylic acid. Such acrylic acid-based polymers which are useful herein are the water-soluble salts of polymerized acrylic acid. The average molecular weight of such polymers in the acid form preferably ranges from about 2,000 to about 10,000, more preferably from about 4,000 to about 7,000, and most preferably from about 4,000 to 5,000. Water-soluble salts of such acrylic acid polymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Suitable polymers of this type are known materials. Use of polyacrylates of this type in detergent compositions has been disclosed, for example, in Diehl, U.S. Pat. No. 3,308,067, issued Mar. 7, 1967.

Acrylic/maleic-based copolymers may also be used as a preferred component of the dispersing/anti-redeposition agent. Such materials include the water-soluble salts of copolymers of acrylic acid and maleic acid. The average molecular weight of such copolymers in the acid form preferably ranges from about 2,000 to about 100,000. A preferred copolymer has an average molecular weight of about 2,000 to 15,000, more preferably about 6,000 to about 13,000, and most preferably about 7,000 to about 12,000. Other preferred copolymers have an average molecular weight from about 5,000 to 75,000, most preferably from about 7,000 to 65,000. The ratio of acrylic to maleate segments in such copolymers will generally range from about 3:1 to about 1:2, more preferably from about 10:1 to 1:1, and most preferably about 2.5:1 to 1:1. Water-soluble salts of such acrylic acid/maleic acid copolymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble acrylic/maleate copolymers of this type are known materials which are described in European Patent Application No. 66915, published Dec. 15, 1982, as well as in EP 193,360, published Sep. 3, 1986, which also describes such polymers comprising hydroxypropylacrylate. Still other useful dispersing agents include the maleic/acrylic/vinyl alcohol terpolymers. Such materials are also disclosed in EP 193,360, including, for example, the 45/45/10 terpolymer of acrylic/maleic/vinyl alcohol.

Particularly preferred dispersant polymers are low molecular weight modified polyacrylate copolymers. Such copolymers contain as monomer units: a) from about 90% to about 10%, preferably from about 80% to about 25% by weight acrylic acid or its salts and b) from about 10% to about 90%, preferably from about 20% to about 80% by weight of a substituted acrylic monomer or its salt and have the general formula: \(-\{(R)^{2}/(R)^{3}/(C(O)/OR)^{3}\}\) wherein the incomplete valencies inside the square braces are hydrogen and at least one of the substituents R\(^1\), R\(^2\) or R\(^3\), preferably R\(^1\) or R\(^2\), is a 1 to 4 carbon alkyl or hydroxalkyl group, R\(^2\) or R\(^3\) can be a hydrogen or alkali metal salt. Most preferred is a substituted acrylic monomer wherein R\(^1\) is methyl, R\(^2\) is hydrogen and R\(^3\) is sodium.

The low molecular weight polyacrylate dispersant polymer preferably has a molecular weight of less than about 15,000, preferably from about 500 to about 10,000, most preferably from about 1,000 to about 5,000. The most preferred polyacrylate copolymer for use herein has a molecular weight of 3500 and is the fully neutralized form of the polymer comprising about 70% by weight acrylic acid and about 30% by weight methacrylic acid.

Other suitable modified polyacrylate copolymers include the low molecular weight copolymers of unsaturated aliphatic carboxylic acids disclosed in U.S. Pat. Nos. 4,530,766, and 5,084,535; both incorporated herein by reference. Agglomerated forms of the present invention may employ aqueous solutions of polymer dispersants as liquid binders for making the agglomerate (particularly when the composition consists of a mixture of sodium citrate and sodium carbonate). Especially preferred are polyacrylates with an average molecular weight of from about 1,000 to about 10,000, and acrylate/maleate or acrylate/fumarate copolymers with an average molecular weight of from about 2,000 to about 80,000 and a ratio of acrylate to maleate or fumarate segments of from about 30:1 to about 1:2. Examples of such copolymers based on a mixture of unsaturated mono- and dicarboxylic acids or esters are disclosed in European Patent Application No. 66,915, published Dec. 15, 1982, incorporated herein by reference.

Other dispersant polymers useful herein include the polyethylene glycols and polypropylene glycols having a molecular weight of from about 950 to about 30,000 which can be obtained from the Dow Chemical Company of Midland, Mich. Such compounds for example, having a melting point within the range of from about 30° C. to about 100° C. can be obtained at molecular weights of 1450, 3400, 4500, 6000, 7400, 9500, and 20,000. Such compounds are formed by the polymerization of ethylene glycol or propylene glycol with the requisite number of moles of ethylene or propylene oxide to provide the desired molecular weight and melting point of the respective polyethylene glycol and polypropylene glycol. The polyethylene, polypropylene and mixed glycols are referred to using the formula \(\text{HO}(\text{CH}_2\text{CH}_2\text{O})_m\text{CH}_2\text{CH}(\text{CH}_3)\text{O}_n\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}\) wherein m, n, and o are integers satisfying the molecular weight and temperature requirements given above.

Yet other dispersant polymers useful herein include the cellulose sulfate esters such as cellulose acetate sulfate, cellulose sulfate, hydroxyethyl cellulose sulfate, methylecellulose sulfate, and hydroxypropylcellulose sulfate. Sodium cellulose sulfate is the most preferred polymer of this group.
Other suitable dispersant polymers are the carboxylated polysaccharides, particularly starches, celluloses and alginates, described in U.S. Pat. No. 3,723,322, Diehl, issued Mar. 27, 1973; the dextrin esters of polycarboxylic acids disclosed in U.S. Pat. No. 3,929,107, Thompson, issued Nov. 11, 1975; the hydroxyalkyl starch ethers, starch esters, oxidized starches, dextrins and starch hydrolysates described in U.S. Pat. No. 3,803,285, Jensen, issued Apr. 9, 1974; the carboxylated starches described in U.S. Pat. No. 3,629,121, Eldrid, issued Dec. 21, 1971; and the dextrin starches described in U.S. Pat. No. 4,141,841, McDonald, issued Feb. 27, 1979; all incorporated herein by reference. Preferred cellulose-derived dispersant polymers are the carboxymethyl celluloses.

Yet another group of acceptable dispersants are the organic dispersant polymers, such as polycarboxylates.

Another polymeric material which can be included is polyethylene glycol (PEG). PEG can exhibit dispersing agent performance as well as act as a clay soil removal-antiredeposition agent. Typical molecular weight ranges for these purposes range from about 500 to about 100,000, preferably from about 1,000 to about 50,000, more preferably from about 1,500 to about 10,000.

Polysparparte and polyglutamate dispersing agents may also be used, especially in conjunction with zeolite builders.

In compositions containing detergent builders, it is believed, though it is not intended to be limited by theory, that polymeric dispersing agents enhance overall detergent builder performance, especially zeolite and/or silicate builders, when used in combination with other builders (including lower molecular weight polycarboxylates) by crystal growth inhibition, particulate soil release peptization, and antiredeposition. Dispersing agents such as polysparpartate preferably have a molecular weight (avg.) of about 10,000.

Suds Suppressors—Compounds for reducing or suppressing the formation of suds can be incorporated into the compositions of the present invention. Suds suppression can be of particular importance in the so-called "high concentration cleaning process" as disclosed in U.S. Pat. Nos. 4,484,455 and 4,489,574 and in front-loading European-style washing machines.

A wide variety of materials may be used as suds suppressors, and suds suppressors are well known to those skilled in the art. See, for example, Kirk Othmer Encyclopedia of Chemical Technology, Third Edition, Volume 7, pages 430-447 (John Wiley & Sons, Inc., 1979). One category of suds suppressor of particular interest encompasses mono- and polycarboxylic fatty acid and soluble salts therein. See U.S. Pat. No. 2,954,347, issued Sep. 27, 1960 to Wayne St. John. The monopesaccharides fatty acids and salts thereof used as suds suppressor typically have hydrocarbyl chains of 10 to about 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include the alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts.

The detergent compositions herein may also contain non-surfactant suds suppressors. These include, for example: high molecular weight hydrocarbons such as paraffin, fatty acid esters (e.g., fatty acid triglycerides), fat acid esters of mono-, mono-, di-, and tri-alkylated amino alcohols, aliphatic C_{18}-C_{30} ketones (e.g., stearone), etc. Other suds inhibitors include N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra-alkylamine chlorotriazines formed as products of cytotoxic chloride with two or three moles of a primary or secondary amine containing 1 to 24 carbon atoms, propylene oxide, and monostearyl phosphates such as monostearyl alcohol phosphate ester and monostearyl di-alkali metal (e.g., K, Na, and Li) phosphates and phosphate esters. The hydrocarbons such as paraffin and haloparaffin can be utilized in liquid form. The liquid hydrocarbons will be liquid at room temperature and atmospheric pressure, and will have a pour point in the range of about -40 °C and about 50 °C, and a minimum boiling point not less than about 110 °C (atmospheric pressure). It is also known to utilize waxy hydrocarbons, preferably having a melting point below about 100 °C. The hydrocarbons constitute a preferred category of suds suppressor for detergent compositions.

Hydrocarbon suds suppressors are described, for example, in U.S. Pat. No. 4,265,779, issued May 5, 1981 to Gandolfi et al. The hydrocarbons, thus, include aliphatic, cyclic, aromatic, and heterocyclic saturated and unsaturated hydrocarbons having from about 12 to about 70 carbon atoms. The term "paraffin," as used in this suds suppressor discussion, is intended to include mixtures of true paraffins and cyclic hydrocarbons.

Another preferred category of non-surfactant suds suppressors comprises silicone suds suppressors. This category includes the use of polyorganosiloxane oils, such as polydimethylsiloxane, dispersions or emulsions of polyorganosiloxane oils or resins, and combinations of polyorganosiloxane with silica particles wherein the polyorganosiloxane is chemisorbed or fused onto the silica. Silicone suds suppressors are well known in the art and are, for example, disclosed in U.S. Pat. No. 4,365,779, issued May 5, 1981 to Gandolfi et al and European Patent Application No. 89037851.9, published Feb. 7, 1990, by Starch, M. S.

Other silicone suds suppressors are disclosed in U.S. Pat. No. 3,455,839 which relates to compositions and processes for defoaming aqueous solutions by incorporating therein small amounts of polydimethylsiloxane fluids.

Mixtures of silicone and silanated silica are described, for instance, in German Patent Application DOS 2,124,526, Silicone defoamers and suds controlling agents in granular detergent compositions are disclosed in U.S. Pat. No. 3,933,672, Bartolotta et al., and in U.S. Pat. No. 4,652,392, Baginski et al, issued Mar. 24, 1987.

An exemplary silicone based suds suppressor for use herein is a suds suppressing agent consisting essentially of:

(i) polydimethylsiloxane fluid having a viscosity of from about 20 cs. to about 1,500 cs at 25 °C;
(ii) from about 5 to about 50 parts per 100 parts by weight of (i) of siloxane resin composed of (CH_{3})_{n}SiO_{1/2} units of SiO_{2} units in a ratio of from 0.5:1 to 1:0.5; and (iii) from about 1 to about 20 parts per 100 parts by weight of (i) of a solid silica gel.

In the preferred silicone suds suppressor used herein, the solvent for a continuous phase is made up of certain polyethylene glycols or polyethylene-polypropylene glycol copolymers or mixtures thereof (preferred), or polypropylene glycol. The primary silicone suds suppressor is branched/crosslinked and preferably not linear.

To illustrate this point further, typical liquid laundry detergent compositions with controlled suds will optionally comprise from about 0.001 to about 1, preferably from about 0.01 to about 0.7, most preferably from about 0.05 to about 0.5, weight % of said silicone suds suppressor, which comprises (1) a nonaqueous emulsion of a primary antifoam agent which is a mixture of (a) a polyorganosiloxane, (b) a resinsiloxane or a silicone resin-producing silicone compound, (c) a finely divided filler material, and (d) a catalyst to promote the reaction of mixture components (a), (b) and (c), to form silanolates; (2) at least one nonionic...
silicone surfactant; and (3) polyethylene glycol or a copolymer of polyethylene-polypropylene glycol having a solubility in water at room temperature of more than about 2 weight %; and without polypropylene glycol. Similar amounts can be used in granular compositions, gels, etc. See also U.S. Pat. Nos. 4,978,471, Starch, issued Dec. 18, 1990, and 4,983,316, Starch, issued Jan. 8, 1991, 5,288,431, Huber et al., issued Feb. 22, 1994, and U.S. Pat. Nos. 4,639,489 and 4,749,740, Aizawa et al at column 1, line 46 through column 4, line 35.

The silicone suds suppressor herein preferably comprises polyethylene glycol and a copolymer of polyethylene glycol/polypropylene glycol, all having an average molecular weight of less than about 1,000, preferably between about 100 and 800. The polyethylene glycol and polyethylene/polypropylene copolymers herein have a solubility in water at room temperature of more than about 2 weight %, preferably more than about 5 weight %.

The preferred surfactant herein is polyethylene glycol having an average molecular weight of less than 1,000, more preferably between about 100 and 800, most preferably between 200 and 400, and a copolymer of polyethylene glycol/polypropylene glycol, preferably PPG 200/PEG 300. Preferred is a weight ratio of between 1:1 and 1:10, most preferably between 1:3 and 1:6, of polyethylene glycol/copolymer of polyethylene-polypropylene glycol.

The preferred silicone suds suppressors used herein do not contain polypropylene glycol, particularly of 4,000 molecular weight. They also preferably do not contain block copolymers of ethylene oxide and propylene oxide, like PLURONIC L101.

Other suds suppressors useful herein comprise the secondary alcohols (e.g., 2-alkyl alkanols) and mixtures of such alcohols with silicone oils, such as the silicones disclosed in U.S. Pat. Nos. 4,798,679, 4,075,118 and EP 150,872. The secondary alcohols include the C_{12}-C_{18} alkyl alcohols having a C_{1}-C_{18} chain. A preferred alcohol is 2-butyl octanol, which is available from Condea under the trademark ISOFOL 12. Mixtures of secondary alcohols are available under the trademark ISALCHEM 123 from Enichem. Mixed suds suppressors typically comprise mixtures of alcohol+silicone at a weight ratio of 1:5 to 5:1.

For any detergent compositions to be used in automatic laundry washing machines, suds should not form to the extent that they overflow the washing machine. Suds suppressors, when utilized, are preferably present in a “suds suppressing amount”. By “suds suppressing amount” is meant that the formulator of the composition can select an amount of this suds controlling agent that will sufficiently control the suds to result in a low-sudsing laundry detergent for use in automatic laundry washing machines.

The compositions herein will generally comprise from 0% to 100% of water. When used as suds suppressors, monoblock fatty acids, and salts therein, will be present typically in amounts up to about 5%, by weight, of the detergent composition. Preferably, from about 0.5% to about 3% of fatty monoblock carboxylic acids suppressor is utilized. Silicone suds suppressors are typically utilized in amounts up to about 2.0%, by weight, of the detergent composition, although higher amounts may be used. This upper limit is practical in nature, due primarily to concern with keeping costs minimized and effectiveness of lower amounts for effectively controlling sudsing. Preferably from about 0.01% to about 1% of silicone suds suppressor is used, more preferably from about 0.25% to about 0.5%. As used herein, these weight percentage values include any silica that may be utilized in combination with polyorganosiloxane, as well as any adjunct materials that may be utilized. Monostearyl phosphate suds suppressors are generally utilized in amounts ranging from about 0.1% to about 2%, by weight, of the composition. Hydrocarbon suds suppressors are typically utilized in amounts ranging from about 0.01% to about 5%, although higher levels can be used. The alcohol suds suppressors are typically utilized at 0.2%–3% by weight of the finished compositions.

Brightening—Any optical brighteners or other brightening or whitening agents known in the art can be incorporated at levels typically from about 0.05% to about 1%, by weight, into the detergent compositions herein. Commercial optical brighteners which may be useful in the present invention can be classified into subgroups, which include, but are not necessarily limited to, derivatives of stilbene, pyrazoline, coumarin, carboxylic acid, methinecyanines, dibenzothiophene-5,5-dioxide, azolene, 5- and 6-membered-ring heterocycles, and other miscellaneous agents. Examples of such brighteners are disclosed in "The Production and Application of Fluorescent Brightening Agents", M. Zahr-adnik, Published by John Wiley & Sons, New York (1982). Specific examples of optical brighteners which are useful in the present compositions are those identified in U.S. Pat. No. 4,790,856, issued to Wilson on Dec. 13, 1988. These brighteners include the PHORWHITE series of brighteners from Verona. Other brighteners disclosed in this reference include: Tinopal UNPA, Tinopal CBS and Tinopal SMB; available from Ciba-Geigy; Artic White CC and Artic White CWD, available from ICI-Lutton-Davis, located in Italy; the 2-(4-styryl-phenyl)-2H-napthol[1,2-d]triazoles; 4,4'-bis(1,2,3-triazol-2-yl)-stilbenes; 4,4'-bis(styryl)bisphenyls; and the aminocoumarins. Specific examples of these brighteners include 4-methyl-7-diyethyl amino coumarin; 1,2-bis(-venzimidazol-2-yl)ethylene; 1,3-diphenyl-phenalazines; 2,5-bis(benzoazol-2-yl)thiophene; 2-styrylnaph[1,2-d]oxazole; and 2-stilbene-4-yl)-2H-naphtho-[1,2-d]triazole. See also U.S. Pat. No. 3,644,015, issued Feb. 29, 1972 to Hamilton. Anionic brighteners are preferred herein.

Chelating Agents—The detergent compositions herein may also optionally contain one or more iron and/or manganese chelating agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

Amino carboxylates useful as optional chelating agents include ethylenediaminetetraacetates, N-hydroxyethyl-ethylenediaminetetraacetates, nitrilotriacetates, ethylenediamine tetraacetates, triethylenetetraminehexacetates, diethylethlenediaminetetraacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetraakis (methyl-eneposphonates) as DEQUEST. Preferred, these amino phosphonates to not contain alkyl or alkyl groups with more than about 6 carbon atoms.

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Pat. No. 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxysulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.
A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer as described in U.S. Pat. No. 4,704,233, Nov. 3, 1987, to Hartman and Perkins. If utilized, these chelating agents will generally comprise from about 0.1% to about 0.5% by weight of the detergent compositions herein. More preferably, if utilized, the chelating agents will comprise from about 0.1% to about 3.0% by weight of such compositions.

Fabric Softening Clay:

Various clay through-the-wash fabric softeners, especially the impervious smectite clays of U.S. Pat. No. 4,062,647, Storm and Nirschl, issued Dec. 13, 1977, as well as other softener clays known in the art, can optionally be used at levels of from about 0.5% to about 0.5% by weight in the present compositions to provide fabric softener benefits concurrently with fabric cleaning. Clay softeners can be used in combination with amine and cationic antistatic agents, as disclosed, for example, in U.S. Pat. No. 4,375,416, Crisp et al, Mar. 1, 1983 and U.S. Pat. No. 4,291,071, Harris et al, issued Sep. 22, 1981.

The clay softening system herein will comprise a fabric softening clay present in an amount of at least 0.5%, preferably from 1% to 30% by weight of the detergent composition. The preferred clays are of the smectite type, although other types of softening clays are known and may be used herein. The following describes non-limiting examples of softening clays.

Smectite type clays are widely used as fabric softening ingredients in detergent compositions. Most of these clays have a cation exchange capacity of at least 50 meq/100 g. Smectite clays can be described as three-layer expandable materials, consisting of alumino-silicates or magnesium silicates.

There are two distinct classes of smectite-type clays; in the first, aluminum oxide is present in the silicate crystal lattice, in the second class of smectites, magnesium oxide is present in the silicate crystal lattice.

The general formulas of these smectites are $\text{Al}_x\text{Si}_y\text{O}_{2x+y}\text{OH}_2$ and $\text{Mg}_x\text{Si}_y\text{O}_{2x+y}\text{OH}_2$, for the aluminum and magnesium oxide type clay, respectively. The range of the water of hydration can vary with the processing to which the clay has been subjected. Furthermore, atom substitution by iron and magnesium can occur within the crystal lattice of the smectites, while metal cations such as Na⁺, Ca²⁺, as well as H⁺ can be co-present in the water of hydration to provide electrical neutrality.

It is customary to distinguish between clays on the basis of one cation predominantly or exclusively absorbed. For example, a sodium clay is one in which the absorbed cation is predominantly sodium. Such absorbed cations can become involved in equilibrium exchange reactions with cations present in aqueous solutions. In such equilibrium reactions, one equivalent weight of solution cation replaces an equivalent of sodium, for example, and it is customary to measure clay cation exchange capacity in terms of milliequivalents per 100 g of clay (meq/100 g).

The cation exchange capacity of clays can be measured in several ways, including dialysis, by exchange with ammonium ion followed by titration, or by a methylene blue procedure, as set forth in Grimshaw, The Chemistry of Clays, Interscience Publishers, Inc. pp. 264–265 (1971). The cation exchange capacity of a clay mineral relates to such factors as the expandable properties of the clay, the charge of the clay, which in turn, is determined at least in part by the lattice structure, and the like. The ion exchange capacity of clays varies widely in the range from about 2 meq/100 g for kaolinites to about 150 meq/100 g, and greater for certain clays of the montmorillonite variety. Illite clays have an ion exchange capacity somewhat in the lower portion of the range, ca. 26 meq/100 g for an average illite clay.

It has been determined that illite and kaolinite clays, with their relatively low ion exchange capacities, are not useful in the instant compositions. Indeed such illite and kaolinite clays constitute a major component of clay soils. However, smectites, such as nontronite having an ion exchange capacity of approximately 50 meq/100 g; saponite, which has an ion exchange capacity greater than 70 meq/100 g, have been found to be useful fabric softeners.

The smectite clays commonly used for this purpose herein are all commercially available. Such clays include, for example, montmorillonite, volchonskoite, nontronite, hectorite, saponite, sauconite, and vermiculite. The clays herein are available under commercial names such as "footer clay" (clay found in a relatively thin vein above the main bentonite or montmorillonite veins in the Black Hills) and various tradenames such as Thixogel #1 (also, "Thixo-Jell") and Gelwhite GP from Georgia Kaolin Co., Elizabeth, N.J.; Volclay BC and Volclay #325, from American Colloid Co., Skokie, Ill.; Black Hills Bentonite BH 450, from International Minerals and Chemicals; and Veegum Pro and Veegum F, from R. T. Vanderbilt. It is to be recognized that such smectite-type minerals obtained under the foregoing commercial and trade names can comprise mixtures of the various discrete mineral entities. Such mixtures of the smectite minerals are suitable for use herein.

Preferred for use herein are the montmorillonite clays having an ion capacity of 50 to 100 meq/100 g which corresponds to ca. 0.2 to 0.6 layer charge.

Quite suitable are hectorites of natural origin, in the form of particles having the general formula

$$\text{(M}_{3n-1j}\text{Si}_{j}\text{Al}_{i}\text{O}_{2i+3j}\text{OH}_{i+j})^{(-3j)}\text{H}^{+}\text{M}^{n+}$$

wherein $\text{M}^{n+}$ is Al, Fe, or B; or $y=O$; $\text{M}^{n+}$ is a monovalent (n=1) or divalent (n=2) metal ion, for example, selected from Na, K, Mg, Ca or Sr.

In the above formula, the value of $(x+y)$ is the layer charge of the hectorite clay.

Such hectorite clays are preferably selected on the basis of their layer charge properties, i.e., at least 50% is in the range of from 0.23 to 0.31.

More suitable are hectorite clays of natural origin having a layer charge distribution such that at least 65% is in the range of from 0.23 to 0.31.

The hectorite clays suitable in the present composition should preferably be sodium clays, for better softening activity.

Sodium clays are either naturally occurring, or are naturally-occurring calcium-clays which have been treated so as to convert them to sodium-clays. If calcium-clays are used in the present compositions, a salt of sodium can be added to the compositions in order to convert the calcium clay to a sodium clay. Preferably, such a salt is sodium carbonate, typically added at levels of up to 5% of the total amount of clay.

Examples of hectorite clays suitable for the present compositions include Bentonite EW and Macaloid, from NL Chemicals, N.J., U.S.A., and hectorites from Industrial Mineral Ventures.

Other softening clays of various types and classes are disclosed in the literature and may also be used herein.

Anti-Static Agents—Consumers who use fabric softeners have come to expect that fabrics treated therewith will also
be provided with an anti-static benefit. Since softer clays are rather poor anti-stats, the formulator may wish to add an anti-static agent to the compositions herein. Various anti-static agents are known in the art and may be used herein, so long as they do not disadvantageously interact with the other ingredients of the compositions. Quite suitable water-soluble antistatic agents herein include the well-known cationic and quaternary ammonium salts such as C10-C18 trimethyl ammonium chloride, the acid salts of the C10-C14 dimethyl amines, the hydroxy-substituted quats, such as the C10-C18 dimethyl(hydroxyethyl)ammonium chloride, C10-C18 di(hydroxyethyl)methylammonium chloride, lauryl trimethylammonium chloride or bromide, and the like. Such optional anti-stats are preferably used at levels from about 0.15% to about 2.5% of the compositions.

Other Ingredients—A wide variety of other ingredients useful in detergent compositions can be included in the compositions herein, including other active ingredients, carriers, hydrotropes, processing aids, dyes or pigments, solvents for liquid formulations, solid fillers for bar compositions, etc. If high Sudsing is desired, Suds boosters such as the C10-C16 alkanolamides can be incorporated into the compositions, typically at 1% to 10% levels. The C12-C14 monoethanol and diethanol amides illustrate a typical class of such Suds boosters. Use of such Suds boosters with high Sudsing adjunct surfactants such as the amine oxides, betaines and sultaines noted above is also advantageous. If desired, soluble magnesium salts such as MgCl2, MgSO4, and the like, can be added at levels of, typically, 0.1% to 2%, to provide additional Suds and to enhance grease removal performance.

Various detergents ingredients employed in the present compositions optionally can be further stabilized by absorbing said ingredients onto a porous hydrophobic substrate, then coating said substrate with a hydrophobic coating. Preferably, the detergent ingredient is admixed with a surfactant before being absorbed into the porous substrate. In use, the detergent ingredient is released from the substrate into the aqueous washing liquor, where it performs its intended detergent function.

To illustrate this technique in more detail, a porous hydrophobic silica (trademark SIFERNAT D10, DeGussa) is admixed with a proteolytic enzyme solution containing 3% to 5% of C13-15 ethoxylated alcohol (EO 7) nonionic surfactant. Typically, the enzyme/surfactant solution is 2.5X the weight of the silica. The resulting powder is dispersed with stirring in silicone oil (various silicone oil viscosities in the range of 500 to 12,500 can be used). The resulting silicone oil dispersion is emulsified or otherwise added to the final detergent matrix. By this means, ingredients such as the aforementioned enzymes, bleaches, bleach activators, bleach catalysts, photoactivators, dyes, fluorescers, fabric conditioners and hydrolyzable surfactants can be "protected" for use in detergents, including liquid laundry detergent compositions.

Liquid detergent compositions can contain water and other solvents as carriers. Low molecular weight primary or secondary alcohols exemplified by methanol, ethanol, propanol, and isopropanol are suitable. Monoalcohols are preferred for solubilizing surfactant, but polyols such as those containing from 2 to about 6 carbon atoms and from 2 to about 6 hydroxyl groups (e.g., 1,3-propanediol, ethylene glycol, glycercine, and 1,2-propanediol) can also be used. The compositions may contain from 5% to 90%, typically 10% to 50% of such carriers.

Granular detergents can be prepared, for example, by spray-drying (final product density about 520 g/l) or agglomerating (final product density above about 600 g/l) the Base Granule. The remaining dry ingredients can then be admixed in granular or powder form with the Base Granule, for example in a rotary mixing drum, and the liquid ingredients (e.g., nonionic surfactant and perfume) can be sprayed on.

The detergent compositions herein will preferably be formulated such that, during use in aqueous cleaning operations, the wash water will have a pH of between about 6.5 and about 11, preferably between about 7.5 and 10.5. Laundry products are typically at pH 9—11. Techniques for controlling pH at recommended usage levels include the use of buffers, alcalis, acids, etc., and are well known to those skilled in the art.

The following examples illustrate the compositions of this invention, but are not intended to be limiting thereof.

**EXAMPLE I**

A granular laundry detergent of the present invention has the following formula:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>% (Wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na linear C12-15 alkylbenzenesulfonate</td>
<td>12.71</td>
</tr>
<tr>
<td>Na C12-14 alkyl sulfate</td>
<td>5.45</td>
</tr>
<tr>
<td>Na alaminio silicate (zeolite)</td>
<td>25.40</td>
</tr>
<tr>
<td>Na carbonate</td>
<td>5.70</td>
</tr>
<tr>
<td>Na silicate</td>
<td>2.19</td>
</tr>
<tr>
<td>Citric acid</td>
<td>6.00</td>
</tr>
<tr>
<td>Protease (Alcalase)</td>
<td>0.90</td>
</tr>
<tr>
<td>Ammonium sulfate</td>
<td>2.00</td>
</tr>
<tr>
<td>Polycrylic acid</td>
<td>3.27</td>
</tr>
<tr>
<td>Polyethylene glycol 8000</td>
<td>1.40</td>
</tr>
<tr>
<td>Optical brightener</td>
<td>0.27</td>
</tr>
<tr>
<td>Sodium sulfate</td>
<td>25.60</td>
</tr>
<tr>
<td>Redox catalyst*</td>
<td>1.00</td>
</tr>
<tr>
<td>Sodium perborate monohydrate</td>
<td>0.35</td>
</tr>
<tr>
<td>Moisture and misc.</td>
<td>100</td>
</tr>
</tbody>
</table>

*Redox Catalyst - a mesoporous molecular sieve catalyst having pore size of about 40 Angstroms, surface area of greater than 500 m²/g, and containing iron as prepared according to U.S. Pat. No. 5,145,816.

When used at 0.10% concentration for laundering fabrics, excellent dye transfer inhibition performance is achieved.

**EXAMPLE II**

The composition of Example I is modified by replacing the sodium percarbonate with an equivalent amount of sodium perborate and deleting the N-methylglucamide. In an alternate mode, all or part of the TAED bleach activator can be replaced by NOBS bleach activator. The composition of Example I can be modified by substituting the chromium catalyst prepared according to Example 17 of U.S. Pat. No. 5,145,816 for the iron-containing redox catalyst. The composition of Example I can also be modified by substituting a manganese-containing redox catalyst for the iron-containing redox catalyst. This manganese-containing redox cata-
l:yst may be prepared, for example, by adsorbing the Mn(O2)(u-O)2(1,4,7-trimethyl-1,4,7-triazacyclononane) 2(PF6)2, as described in U.S. Pat. No. 5,246,621, according to the process of U.S. Pat. No. 5,145,816; or by adsorbing manganese acetate in place of the chromium acetate of Example 17 of U.S. Pat. No. 5,145,816.

**EXAMPLE III**

A detergent bar is prepared by compacting and extruding a composition generally according to Example I. Where allowed by statute, the zeolite/citrate builder may be
EXAMPLE IV

A dry laundry bleach is as follows:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>% (Wt.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium percarbonate</td>
<td>20.0</td>
</tr>
<tr>
<td>Benzoyl capro lactum activator</td>
<td>10.0</td>
</tr>
<tr>
<td>Redox catalyst**</td>
<td>1.0</td>
</tr>
<tr>
<td>Water-soluble filler**</td>
<td>Balance</td>
</tr>
</tbody>
</table>

*Redox Catalyst - a mesoporous molecular sieve catalyst having pore size of about 40 Angstroms, surface area of greater than 500 m²/g, and containing iron as prepared according to U.S. Pat. No. 5,145,816.
**Sodium carbonate, sodium silicate mixture (1:1).

In each of the preceding examples, compositions are also prepared by substituting as the Redox catalyst the zeolite X manganese (II) bipyridine catalyst, zeolite Y manganese (II) bipyridine catalyst, or mixtures thereof, prepared as described in Knops-Gerrits, et al., “Zeolite-encapsulated Mn(II) complexes as catalysts for selective alkene oxidation”, *Nature*, Vol. 369, pp. 543–546 (Jun. 16, 1994), incorporated herein by reference in its entirety.

What is claimed is:

1. A cleaning composition comprising:
   (a) at least about 0.001% by weight of a large pore size redox catalyst, wherein the large pore size redox catalyst comprises (i) a crystalline silicate or aluminosilicate having a pore size of 20 Angstroms or greater and a surface area of at least about 300 m²/g, and (ii) a physically, ionically, or covalently attached metal selected from the group consisting of manganese, nickel, chromium, copper, tungsten, titanium, cobalt, molybdenum, ruthenium, iron and mixtures thereof;
   (b) a cleaning adjunct ingredient selected from the group consisting of:
      (i) from about 0.001% to about 5%, by weight, of enzymes;
      (ii) from 0.1% to about 80%, by weight, of a detersive surfactant;
      (iii) from about 1% to about 80%, by weight, of a detergent builder;
      (iv) from about 1% to about 30%, by weight, of a bleaching agent; and
      (v) mixtures thereof.

2. A laundry detergent composition comprising:
   (a) at least about 0.001% by weight of a large pore size redox catalyst, wherein the large pore size redox catalyst comprises (i) a crystalline silicate or aluminosilicate having a pore size of 20 Angstroms or greater and a surface area of at least about 300 m²/g, and (ii) a physically, ionically, or covalently attached metal selected from the group consisting of manganese, nickel, chromium, copper, tungsten, titanium, cobalt, molybdenum, ruthenium, iron and mixtures thereof;
   (b) from about 0.001% to about 5%, by weight, of enzymes selected from the group consisting of protease, cellulase, amylase, lipase, peroxidase, and mixtures thereof;
   (c) from about 0.1% to about 80%, by weight, of a detersive surfactant;
   (d) from about 5% to about 30%, by weight, of a detergent builder;
   (e) from about 1% to about 30%, by weight, of a bleaching agent; and
   (f) the balance of the composition comprising detersive adjunct ingredients.

3. A laundry detergent composition according to claim 1, further comprising an enzyme selected from the group consisting of protease, cellulase, amylase, lipase, peroxidase, and mixtures thereof.

4. A composition according to claim 3 which additionally comprises at least about 0.05% by weight of an enzyme stabilizer.

5. A composition according to claim 2 wherein the detersive builder is a non-phosphorus builder selected from the group consisting of zeolites, layered silicates, polycarboxylate builders, and mixtures thereof.

6. A composition according to claim 2 wherein the surfactant is a member selected from the group consisting of alkyl sulfates, alkyl ethoxy sulfates, polyhydroxy fatty acid amides, ethoxylated alcohols, and mixtures thereof.

7. A composition according to claim 2 which further comprises at least about 0.1%, by weight, of a bleach activator.

8. A composition according to claim 2 wherein the bleaching agent is selected from perborates, percarbonates, percarboxylic acids, persulfate, and mixtures thereof.

9. The composition according to claim 1 wherein the large pore size redox catalyst is a liquid crystal template synthesized silicate or aluminosilicate material.

10. A method for cleaning soiled fabrics, comprising contacting said fabrics with an aqueous medium which contains at least about 50 ppm of a composition according to claim 1.

11. A method for cleaning soiled fabrics, comprising contacting said fabrics with an aqueous medium which contains at least about 50 ppm of a composition according to claim 2.

* * * * *